



High Temperature Membrane with Humidification-Independent Cluster Structure

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FuelCell Energy, Inc.

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Project ID #
FC23

Overview

Timeline

- Start: July 2006
- End: May 2011
- 38% complete

Budget

- Total project funding
 - DOE share: \$1500k
 - Contractor share: \$600k
- DOE share spent to date: \$400k
- Funding for FY08: \$225k to date

Barriers

- Low Proton Conductivity at 25-50% Inlet Relative Humidity and 120°C

Partners

- Polymer Partner
 - Polymer & membrane fab. and characterization
- UConn
 - Membrane conductivity and gas crossover
- Consultants
 - Polymer, additives



Acknowledgements

- **DOE: Jason Marcinkoski, Amy Manheim, Reg Tyler, Tom Benjamin and John Kopasz**
- **UCF: Jim Fenton & Team (Testing protocols, membrane conductivity)**
- **BekkTech LLC: Tim Bekkedahl (In-plane conductivity measurement)**
- **FCE Team: Pinakin Patel, Ray Kopp, Jonathan Malwitz, Nikhil Jalani**



FCE Overview

- **Leading fuel cell developer for over 30 years**
 - MCFC, SOFC, PAFC and PEM (up to 2 MW size products)
 - Over 200 million kWh of clean power produced world-wide (>60 installations)
 - Renewable fuels: over two dozen sites with ADG fuel
 - Ultra-clean technology: CARB-2007 certified: Blanket permit in California
- **Highly innovative approach to fuel cell development**
 - Internal reforming technology (45-50% electrical efficiency)
 - Fuel cell-turbine hybrid system (55-65% electrical eff.)
 - Enabling technologies for hydrogen infrastructure
 - Co-production of renewable H_2 and e^- (60-70% eff. w/o CHP)
 - Solid state hydrogen separation and compression
- **High temp. membrane: leverage existing experience in composite membranes for other fuel cell systems (PAFC, MCFC, SOFC)**



Danbury, CT



Torrington, CT



Approach for the Composite Membrane

Target Parameter	DOE Target (2010)	Approach
Conductivity at: 120°C	100 mS/cm	Multi-component composite structure, lower EW
: Room temp.	70 mS/cm	Higher number of functional groups
: -20°C	10 mS/cm	Stabilized nano-additives
Inlet water vapor partial pressure	1.5 kPa	Immobilized cluster structure
Hydrogen and oxygen cross-over at 1 atm	2 mA/cm ²	Stronger membrane structure; functionalized additives
Area specific resistance	0.02 Ωcm ²	Improve bonding capability for MEA
Cost	<40 \$/m ²	Simplify polymer processing
Durability: <ul style="list-style-type: none"> - with cycling at >80°C - with cycling at ≤80°C 	>2000 hours >5000 hours	Thermo-mechanically compliant bonds, higher glass transition temperature
Survivability	-40°C	Stabilized cluster structure design



Technical Accomplishments

- Performed 3 iterations of advanced Polymer Membrane; comprehensive characterization
- Multi-Component Composite (**mC²**) membrane: synthesized >20 batches
- Three different additives for water retention and protonic conductivity enhancement have been fabricated and tested
- Conductivity measurements: >20 samples analyzed, incl. 9 samples verified by BekkTech. Results are encouraging
- Conductivity is used as a “progress marker”; cell test provides a more realistic picture

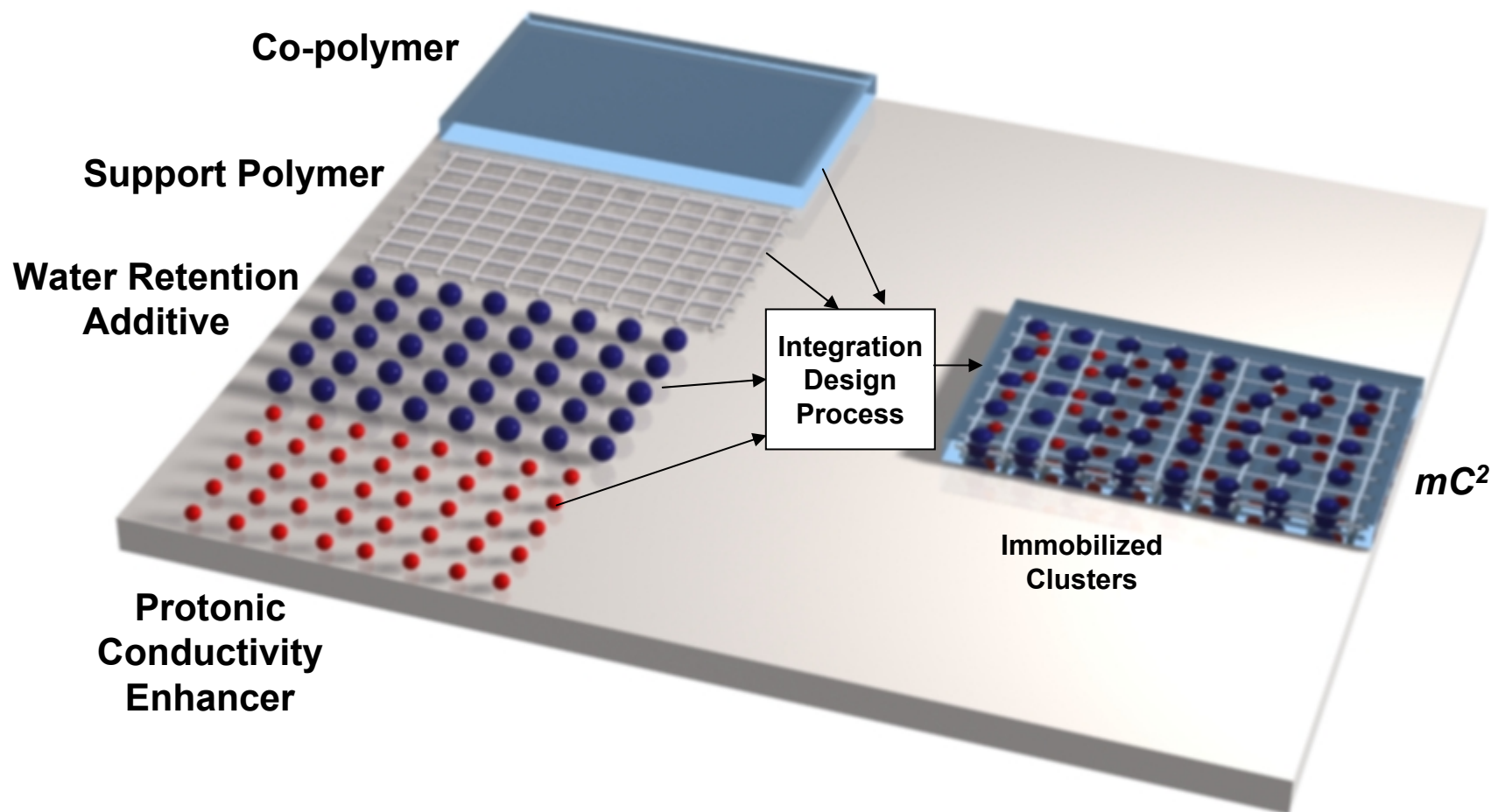


Technical Milestone Status

- Baseline membrane material and processing technique selected (6 month milestone met)
- Screened promising additives for baseline composite membrane (12 month milestone met)
- Baseline membrane fully characterized (18 month milestone met)
- Advanced Membrane material/composition/processing defined (18 month milestone met)
- 0.07 S/cm at 80% RH at R.T. (21 month milestone met)



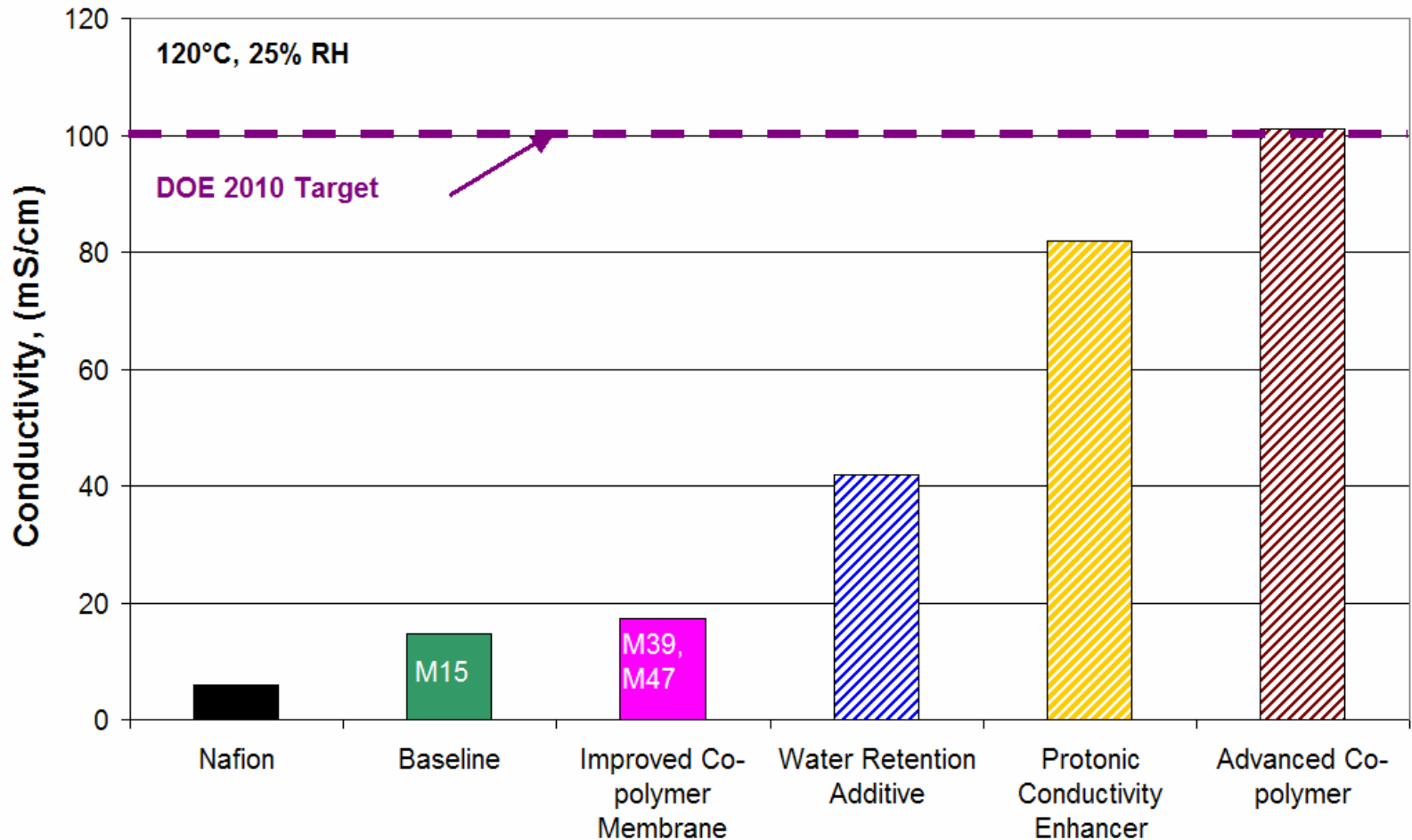
Composite Membrane Concept



Multi-Component System with Functionalized Additives



Development Steps to Conductivity Goal



Membrane Conductivity Improvements Progressed as Planned



Proton Transport in Composite Membrane

Surface (requires
chemically bound water)

Grotthuss (requires
free water)

Additive
Contribution

$$\sigma_p = \sigma_{H^+}^{\Sigma} + \sigma_{H^+}^G + \sigma_{H^+}^E + \sigma_{H^+}^A$$

$$\sigma_{H^+}^{\alpha} = \frac{F^2}{RT} D_{H^+}^{\alpha} C_{H^+}^{\alpha}$$

$$\sigma_p = \frac{\varepsilon}{\tau} \left[\frac{F^2}{RT} \left\{ D_{H^+}^{\Sigma} C_{H^+}^{\Sigma} + \left(D_{H^+}^G + \frac{D_{H^+W}}{1+\delta} \right) C_{H^+} \right\} \right] + \frac{\varepsilon_A}{\tau_A} \left[\frac{F^2}{RT} D_{H^+}^A C_{H^+}^A \right]$$

$C_{H^+}^{\Sigma}$ and C_{H^+} obtained from sorption thermodynamics

Maintaining High Proton Concentration and High Mobility are Focused



Mechanical Properties: Nafion vs. Baseline and Improved

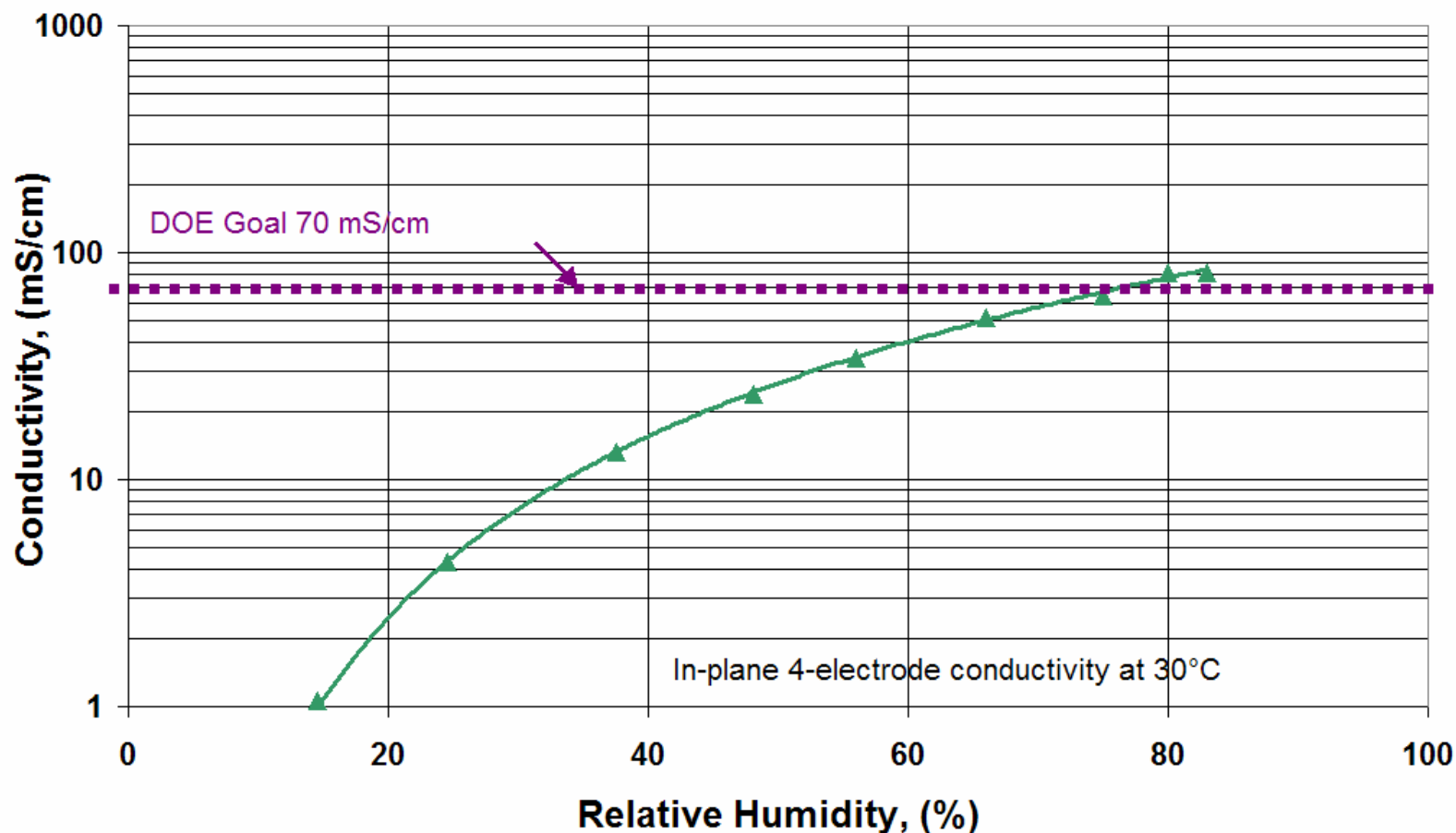
ASTM D638, 23°C, 50% RH

Membrane (Dry state)	N112		Baseline M15		Improved M39	
Test direction	MD	TD	MD	TD	MD	TD
Tensile Modulus, MPa	232	208	182	188	209	220
Tensile Strength, MPa	38	23	34	24	23	24
Elongation at Break, %	117	228	162	214	141	195

Mechanical Strength is Maintained



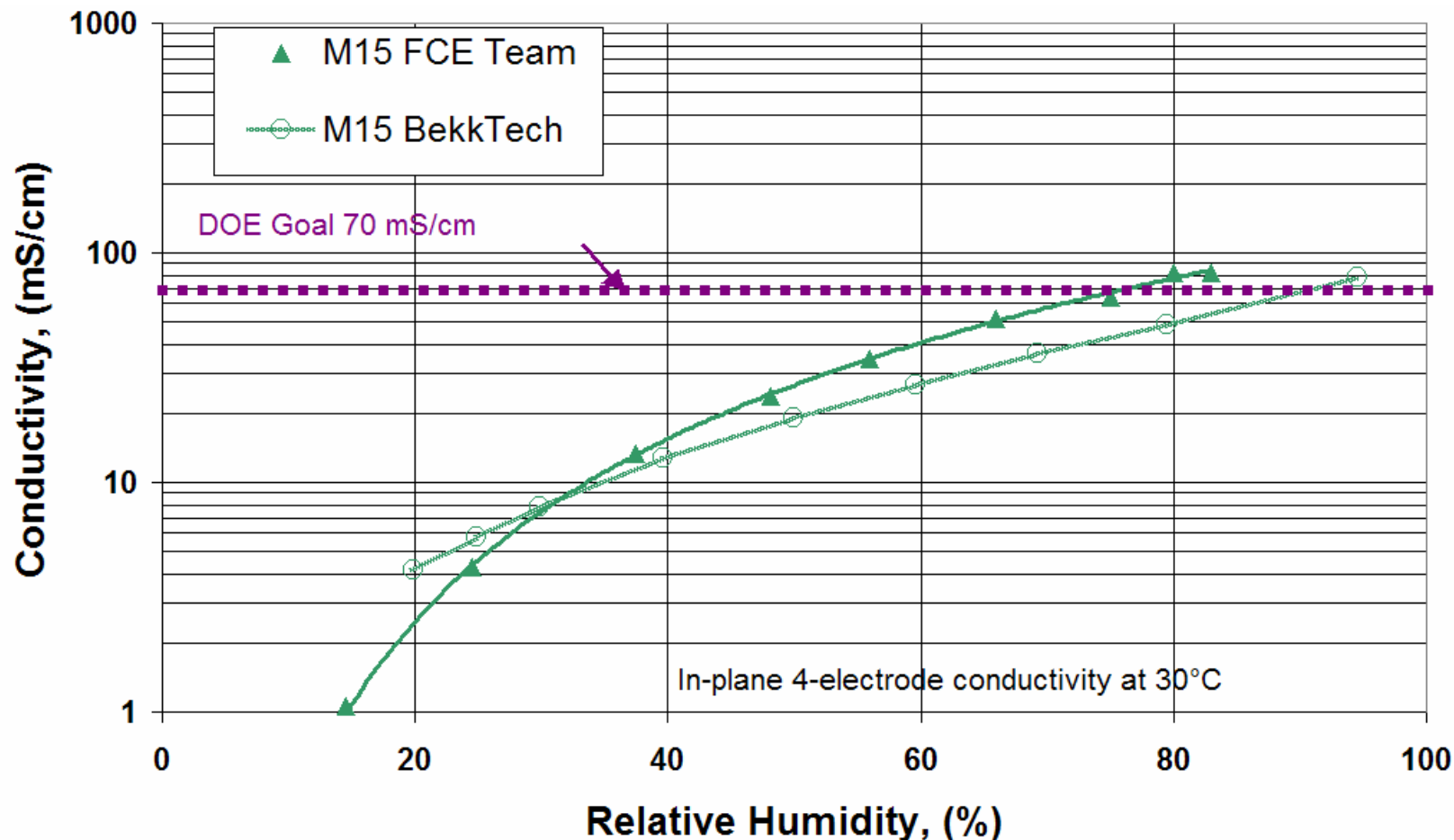
Membrane Conductivity at R.T.: FCE Data



DOE Room Temperature Conductivity Target Met



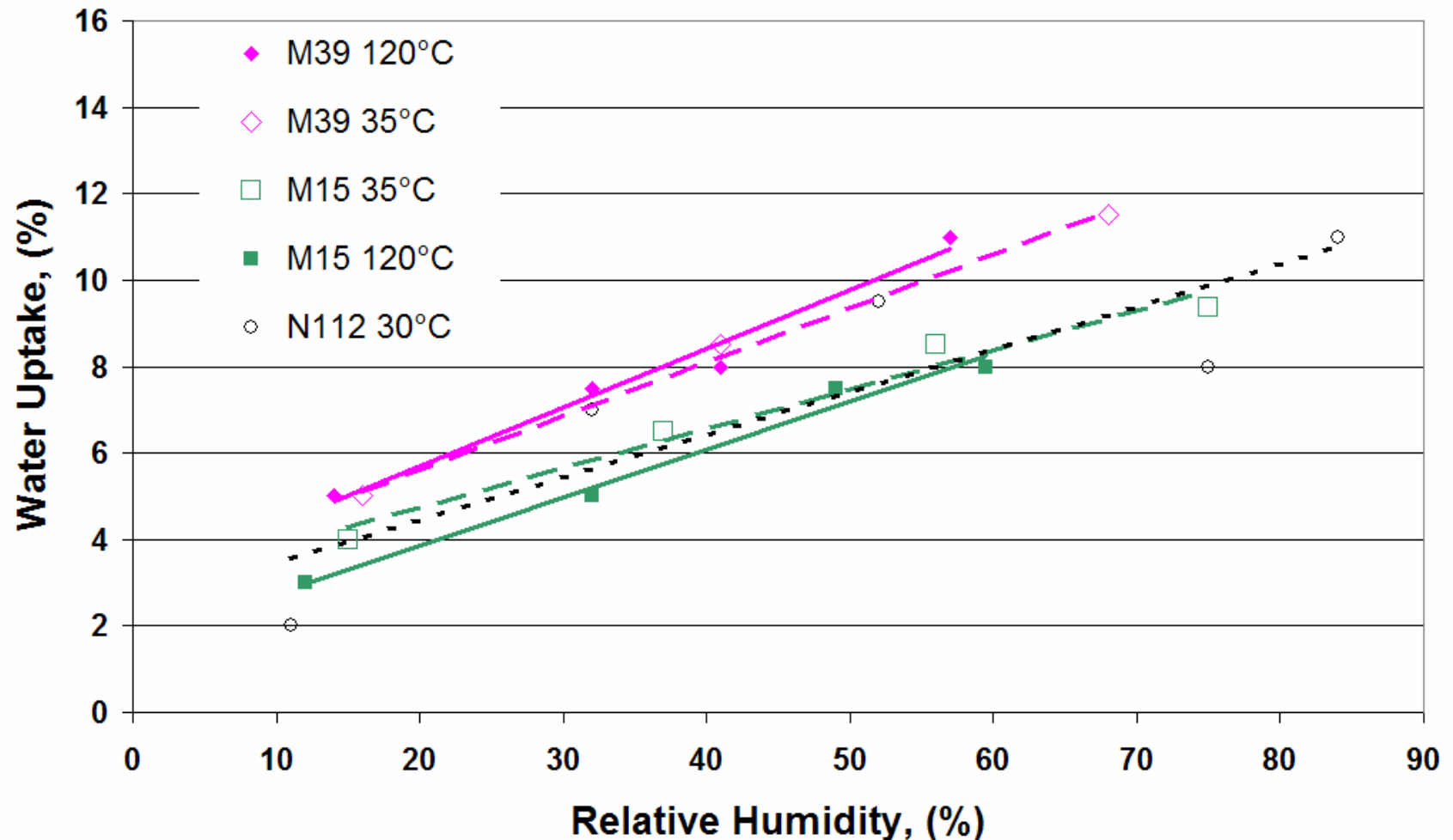
Membrane Conductivity at R.T.: Validation



**Rationalizing Differences in Measurement Results
(Variability in Water Content during Measurement)**



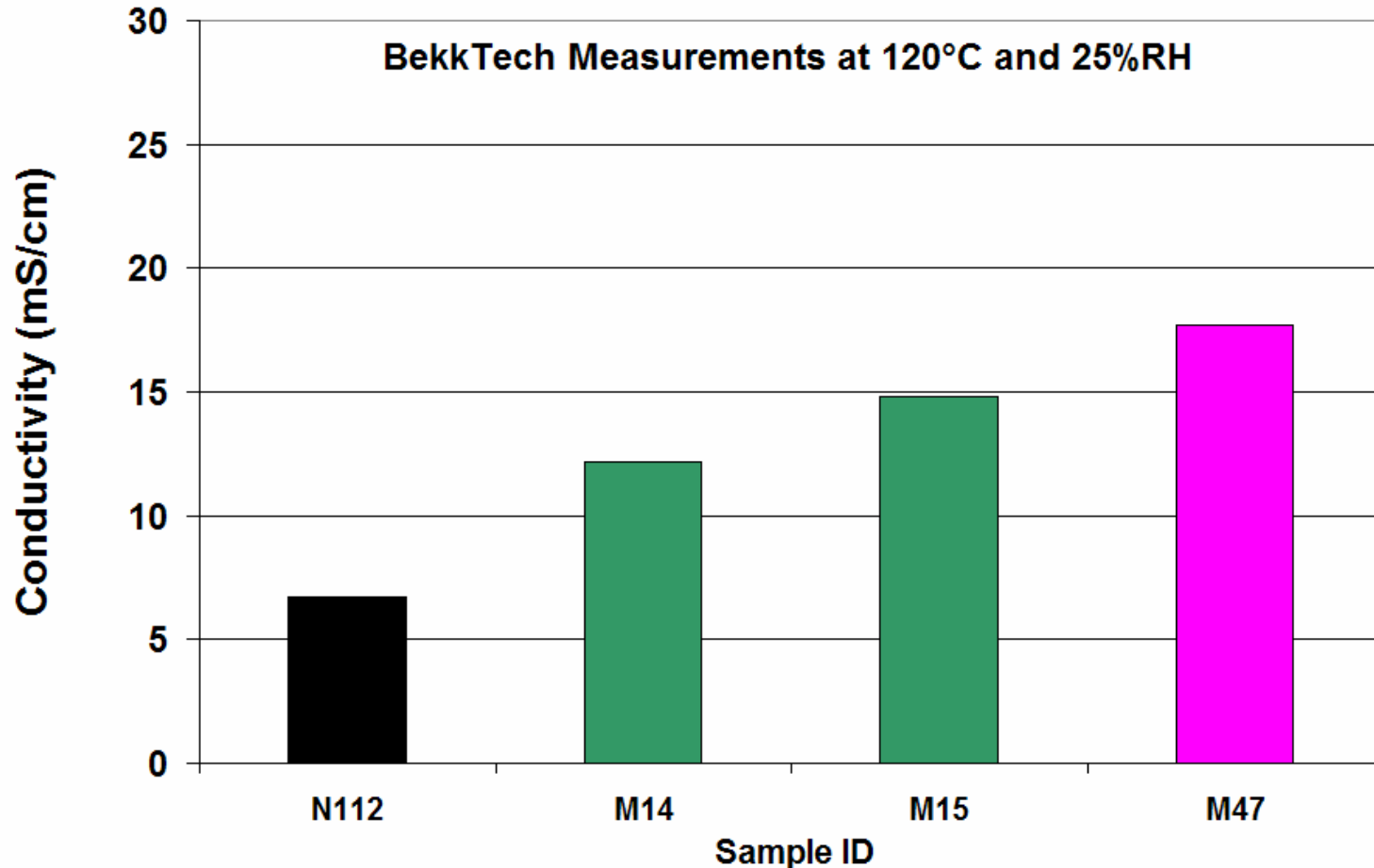
Membrane Water Uptake



~50% Increase in Water Uptake Compared to N112



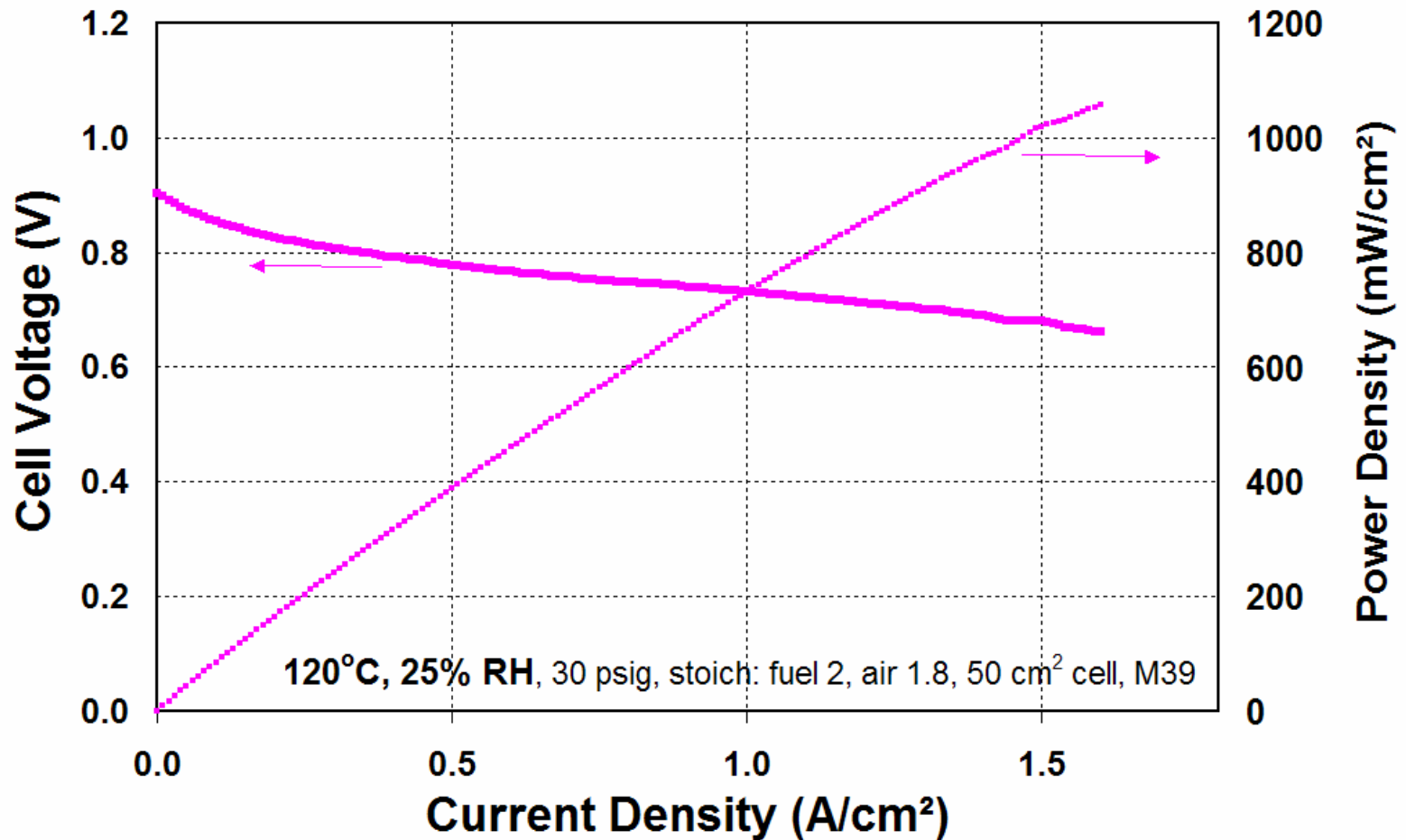
In-Plane Conductivity at 120°C 25% RH



Almost 3x Improved Membrane Conductivity vs. N112



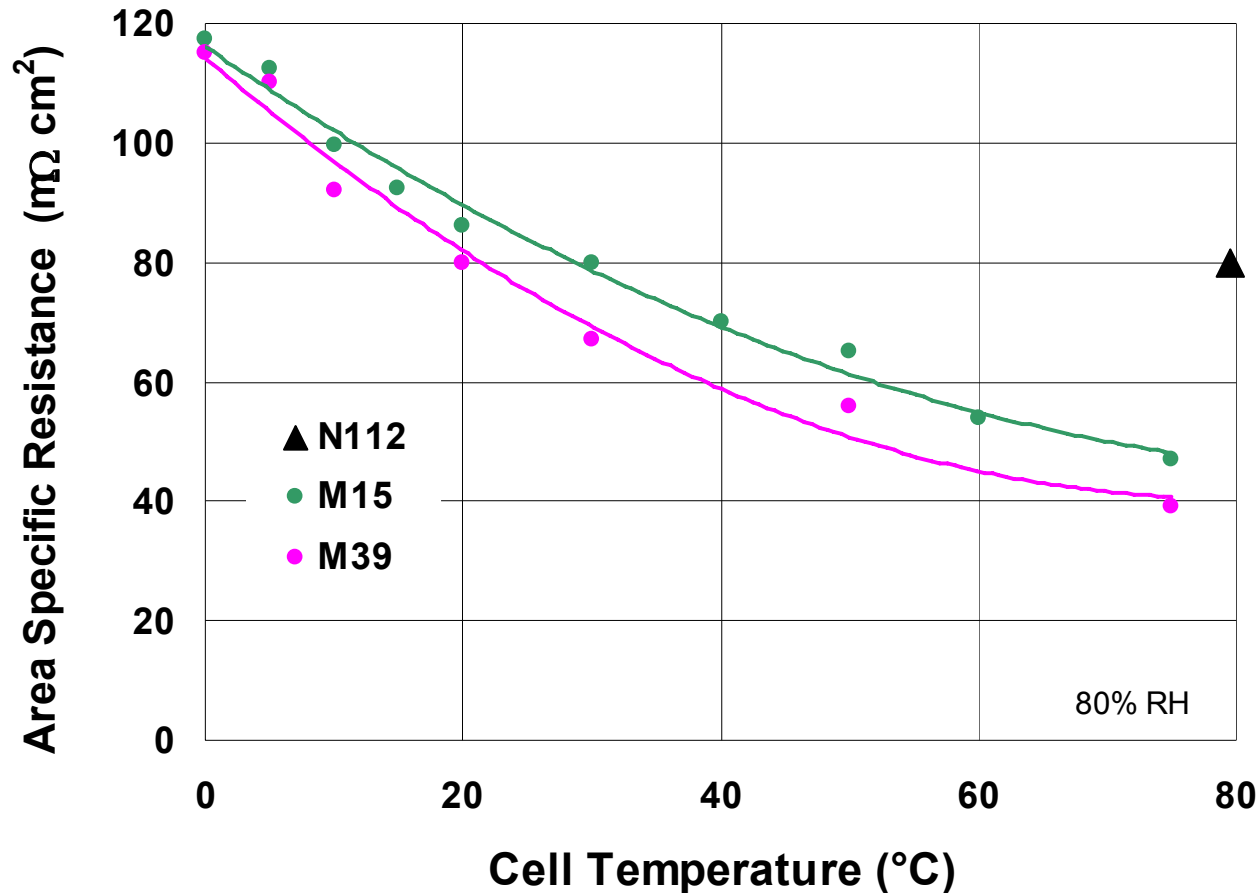
Cell Performance at 120°C and 25% RH



High Cell Performance Achieved



Area Specific Resistance



- Low Area Specific Resistance (ASR) Achieved
- Improved Membrane has Lower ASR than Baseline, as Expected



Membrane Additive Development

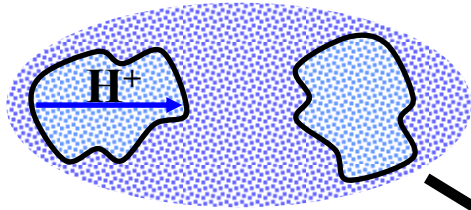
- Benefits:**
- Conductivity less dependent on RH
 - Conductivity at subfreezing temp.
 - Potentially lower cost
 - Design for mechanical strength

- Anticipated Issues:**
- Water solubility
 - Electrochemical stability
 - Compete for “real estate”
 - Additive particle size
 - Non-uniform dispersion

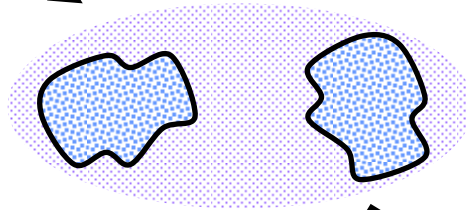


Membrane Additive Development

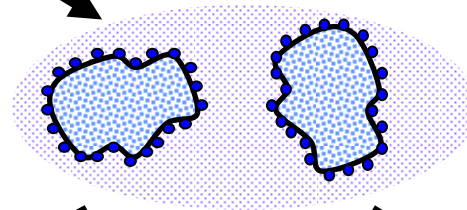
High RH



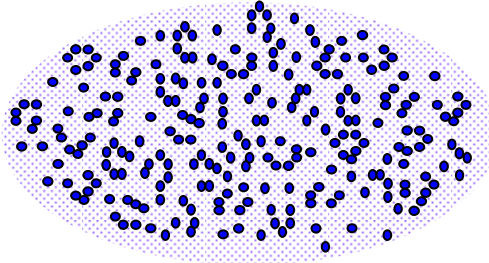
Low RH



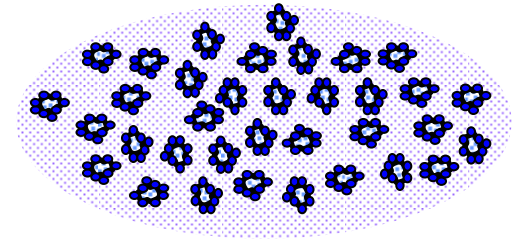
Functionalized Additive



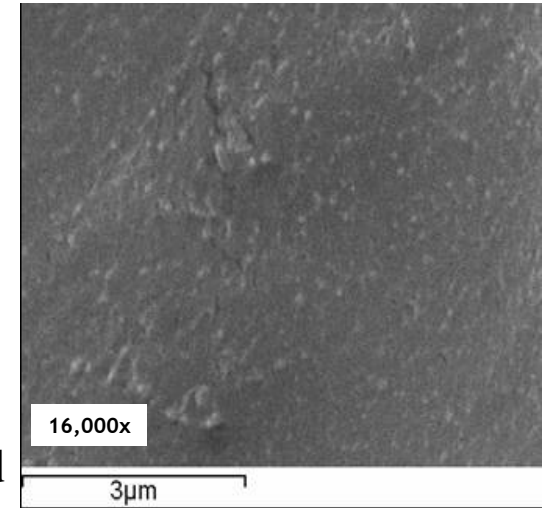
Unsupported Proton Conductor



Smaller Particles



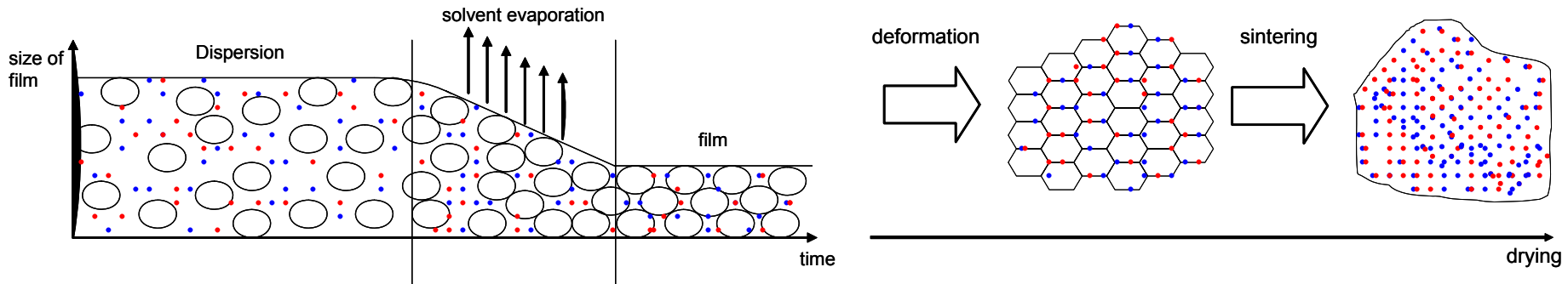
(Higher Surface Area) 19



Strategy for retaining water and increasing conductivity at low RH



Composite Membrane Processing: Casting



Critical steps in membrane casting:

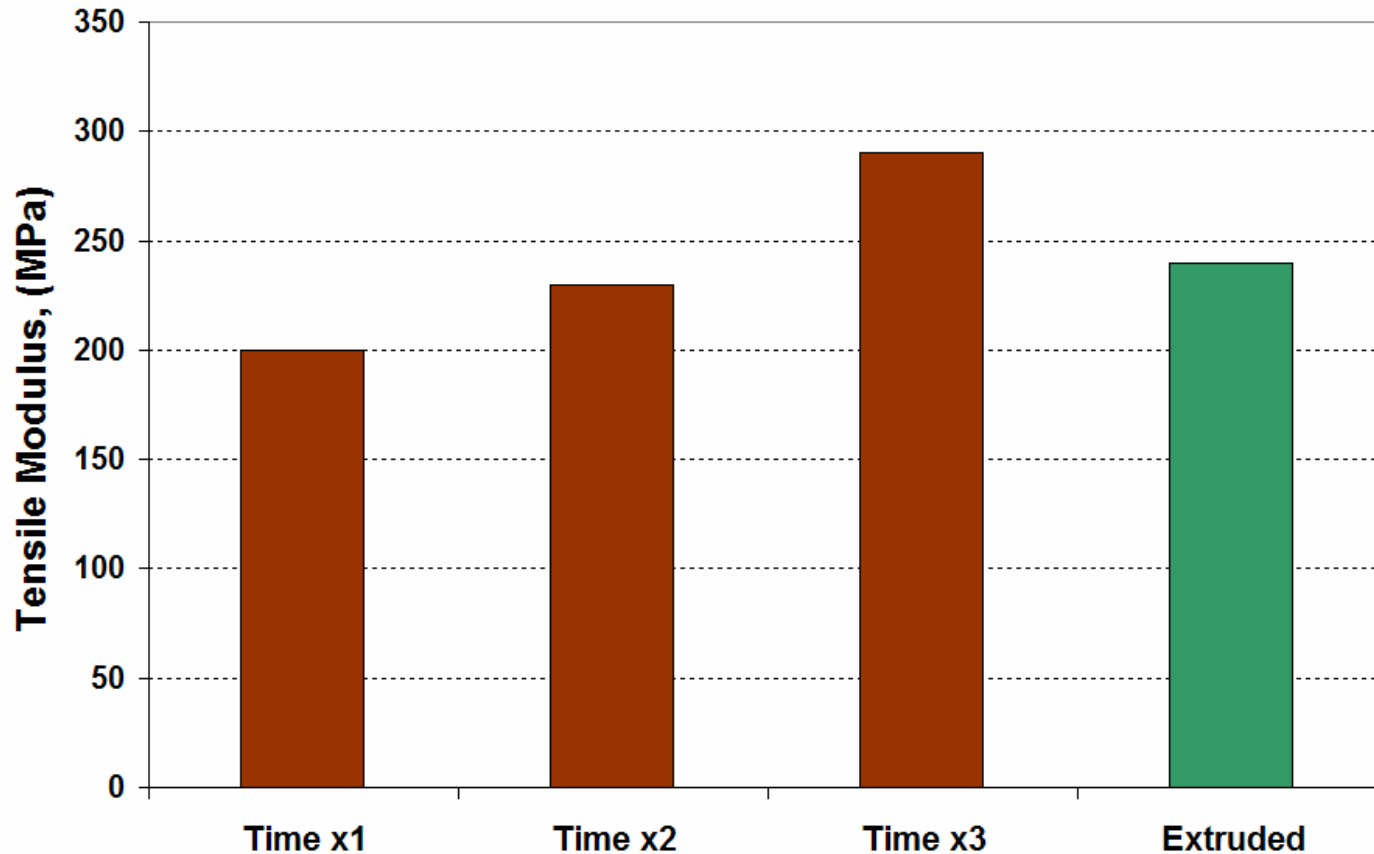
- Evaporation (Time, Temp.)
- Sintering (Time, Temp.)

Preliminary results of parametric analysis:

- Resistance to dissolution increases with time & T
- Membrane resistance increases with time and temp.
- Hydrogen permeability largely unaffected



Cast Membrane Mechanical Properties

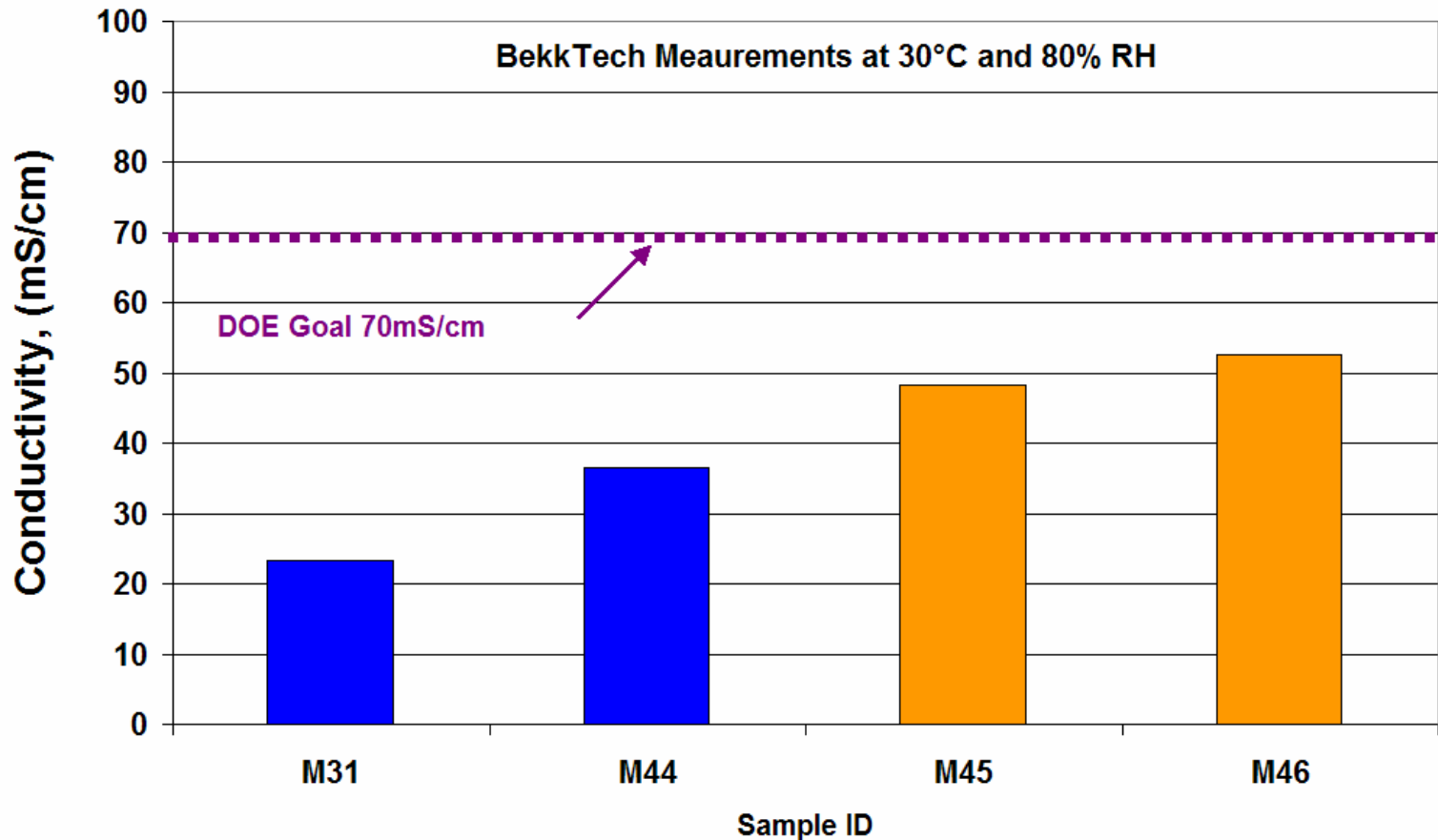


- Cast Membrane Modulus Comparable to Extruded
- Longer Sintering Time Improves Modulus



Composite Membr. Conductivity at R.T.

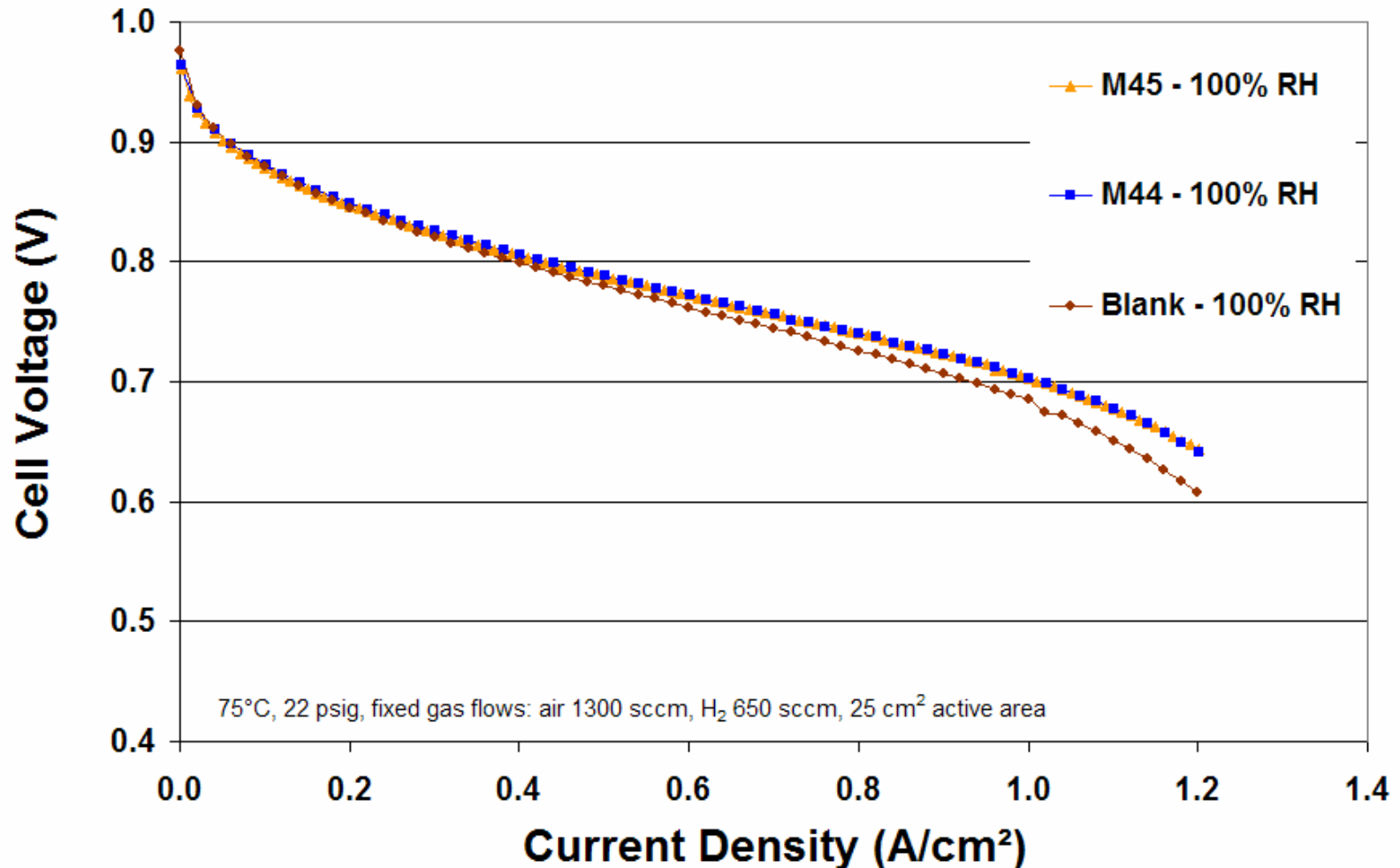
BekkTech Test Data



Significant Progress is Being Made in the mC² Process



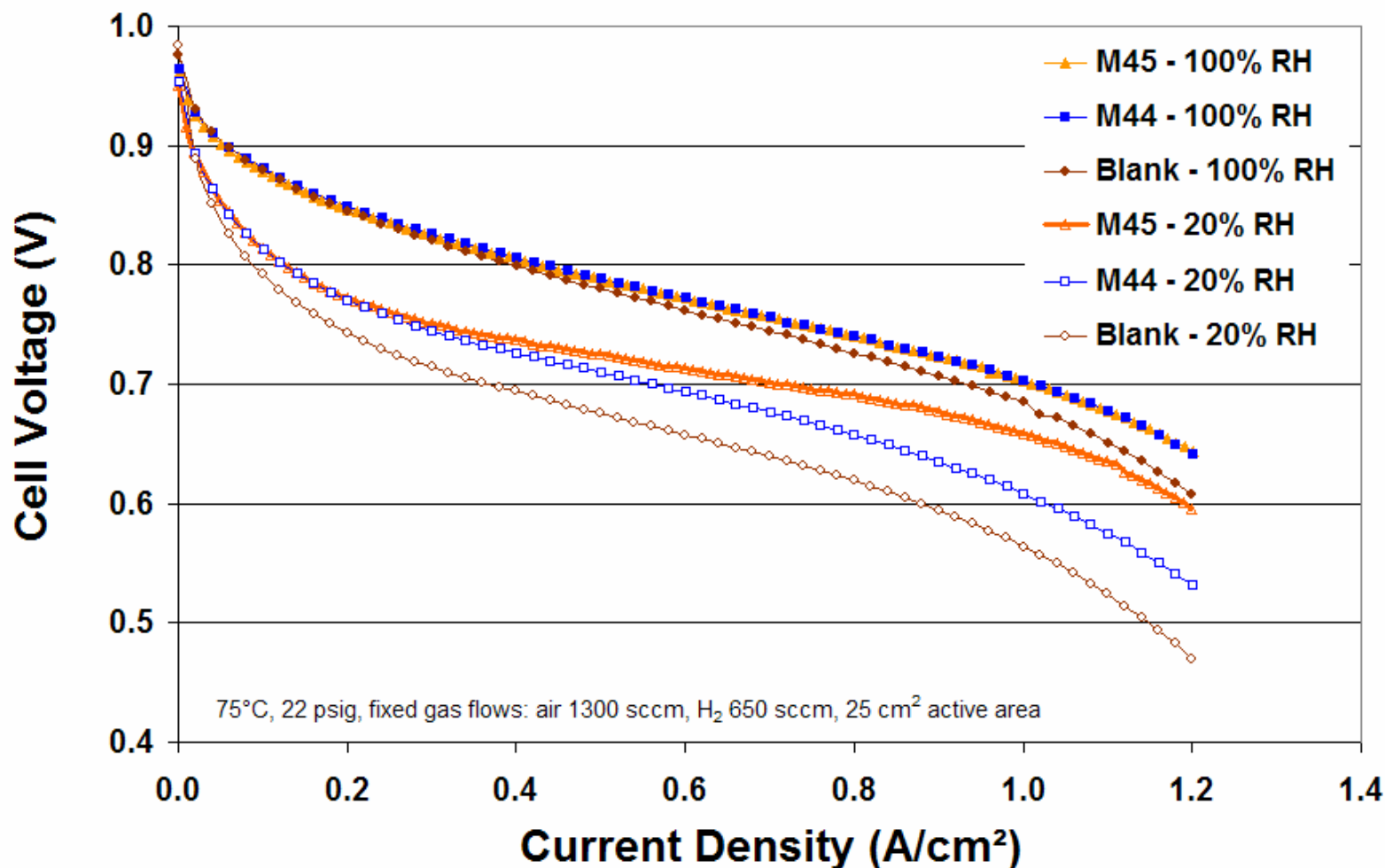
Composite Membrane Cell Testing: 100% RH



Performance is Comparable at 100% RH



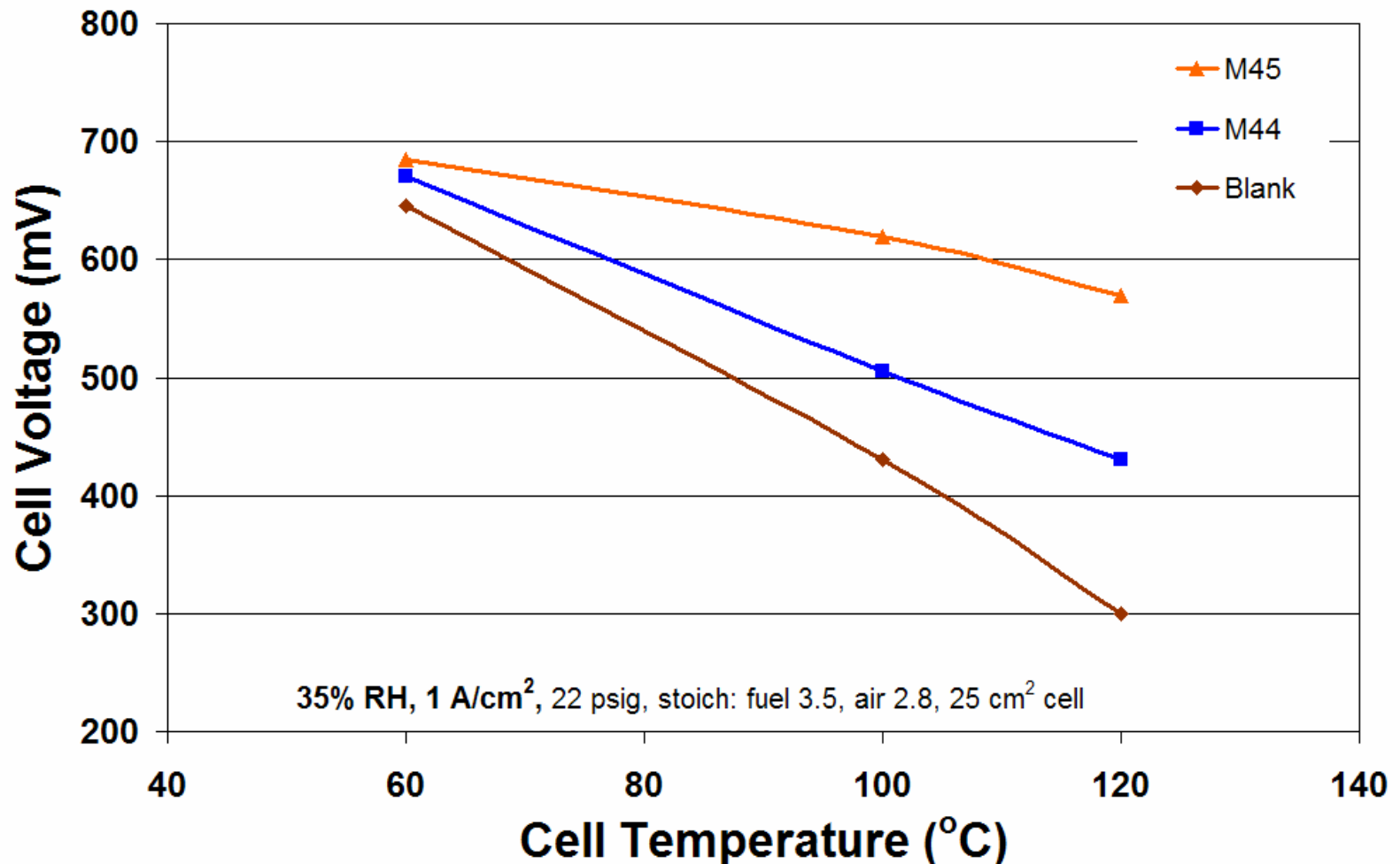
Composite Membrane Cell Testing: 20% RH



mC² Shows ~50% Improvement Compared to Blank



Composite Membrane Performance as f(T)



**Additives Effective in Maintaining Good Cell Performance
at High Temperature and Low RH**



Future Work

- **Improve additive dispersion**
- **Optimize composite membrane processing conditions for additives**
- **Study effect of additive loading**
- **Gas permeation and conductivity measurements**
- **Durability Testing:**
 - **RH Cycling**
 - **OCV Testing**
 - **Single cell testing**
- **Pursuing collaboration with OEM**



Future Work

- **Upcoming Key Milestones:**
 - **Select preferred design for the composite membrane (8/08)**
 - **Meet conductivity target of 100 mS/cm at 50% RH at 120°C (5/09 Go/No-Go)**
 - **Conductivity testing by DOE (annually)**



Project Summary

- **Fabricated 3 polymer iterations, 3 types of additives and >20 composite membr. batches**
- **Demonstrated 20% improved conductivity over 2007 and ~3x higher than Nafion 112[®], without loss in mechanical properties**
- **Composite membrane shows significantly better cell performance at low RH than expected from conductivity tests**
- **Achieved low cell resistance**



Project Summary Table

DOE 2010 Technical Targets for Membranes for Transportation Applications				
Performance Parameter	Units	2010 Target	Standard Membrane (Nafion [®] 112)	FY07-08 Result
Conductivity at 30°C and 80% RH	mS/cm	70	38	56-78
Conductivity at 120°C and 25% RH	mS/cm	100	6.7	17.7

